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(21) International Application Number: PCT/FI92/00305 (22) International Filing Date: 11 November 1992 (11.11.92) (30) Priority data: 915541 25 November 1991 (25.11.91) FI (71) Applicant (for all designated States except US): RAISION TEHTAAT OY AB [FI/FI]; SF-21200 Raisio (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): HAMUNEN, Antti [FI/ FI]; Lumparlankatu 13 C 20, SF-21200 Raisio (FI). NURMI, Kari [FI/FI]; Valopolku 1, SF-21200 Raisio (FI). (74) Agent: OY JALO ANT-WUORINEN AB; Iso Robertinka- tu 4-6 A, SF-00120 Helsinki (FI).		(81) Designated States: CA, DE, GB, NL, SE, US. Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: A METHOD FOR REDUCING THE PERMEABILITY OF PAPER AND BOARD AND A SUBSTANCE FOR THE METHOD (57) Abstract The invention concerns the permeability of paper and board substrate. The permeability of the substrate is reduced by coating it with a modified coating mixture, which is based on a polymer dispersion containing at least one modified starch component. The polymer is prepared preferably by grafting monomers onto the modified starch structure.		

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A method for reducing the permeability of paper and board and a substance for the method

5 The object of this invention is a method for reducing the permeability of paper and board in which state the treated product possesses sufficiently good barrier properties against gases and vapours such as water vapour as required in the packaging industry, for example. Despite possessing this property, paper or board treated in accordance with this method is readily disposable as waste 10 by, for example, composting or recycling the product back as raw material for the fibre-consuming industry (i.e. the product can be re-pulped; i.e. disintegrated into fibrous material without causing problems when used again in papermaking). The invention also involves the 15 substance by means of which the aforementioned properties are achieved.

20 Increasingly strict regulations pertaining to environmental protection have led to a situation in which the manufacturers of packaging materials, for example, are required to organize the post-consumption treatment of the resultant waste in an environment-friendly manner. In other words, packaging waste has to be either recycled to 25 provide industrial raw material or it has to be disposed of by composting, for example. If the latter option is resorted to, then the material as a whole must be biodegradable without releasing any environmentally hazardous chemicals.

30 The above requirements mean that the continued use of conventional solutions (e.g. papers whose non-permeability has been achieved by a plastic film lamination) lead to high costs because of the material's poor degradability and unsuitability for recycling. This is so in packaging 35 situations where the package is required to possess barrier properties against water vapour, for instance. Certain commonly used polymers that possess good barrier

properties (e.g. products containing polyvinyl chloride) cannot be disposed of by burning because of the hazard caused by hydrogen chloride gas and dioxin.

5 The purpose of this invention is to eliminate the above shortcomings and to make available a paper product which, while offering adequate barrier properties, can be re-cycled as raw material for the paper industry or disposed of by composting or left to decompose in landfills, for
10 instance.

The method in accordance with the invention is based on spreading onto the surface of paper or board a dispersion product containing a component that includes modified
15 starch. The said dispersion product can also be spread between the layers making up paper or board in which case the polymer layer formed when the dispersion dries provides the required barrier protection. When spread between the layers, the dispersion also forms an adequate
20 adhesion between the layers and thus no actual gluing treatment is needed.

It is known that papers can be treated with products containing wax dispersions in order to provide them with
25 protection against moisture. It is also known that the said products usually contain commonly used synthetic polymer dispersions such as styrene butadiene, acrylate or polyvinyl acetate latexes that provide the products with adequate adhesion. The proportion of latexes in the
30 total polymer dispersion's solid matter content is generally high. Examples of the above technology are to be found in patent literature; e.g. GB 1 593 331 (J. Vase, Kemi Oy) and the Finnish patent application 901928 (Neusiedler AG) contain descriptions of this technology.

35 The technology in accordance with these inventions provides an adequate barrier against water vapour. However,

seeing as the proportion of latex composed entirely of synthetic substances is high, the product's recyclability is impaired as a result of the latex-based disturbance substance accumulation when such material is made into pulp. On the other hand, if the proportion of wax dispersion is in the vapour barrier substance is raised excessively, the dispersion's adhesive and gluing properties are impaired as is also the printability of the treated surface due to its ink repelling property.

10 The present invention's point of departure has been to avoid the aforementioned shortcomings by preparing the dispersion so that it contains components that promote the disintegration of the synthetic product in nature and
15 during the various stages of recycling processes. This has been executed either (A) by joining natural polymer chains (especially starch) to the latex polymer at the manufacturing stage or (B) by replacing a significant part of the latex polymer with a combination polymer -
20 starch graft copolymer - consisting of starch and a synthetic substance. It has been observed that paper products treated with thus manufactured dispersions are more readily made into pulp than papers treated with latexes made according to conventional recipes. Moreover, the
25 dispersion residuals formed in conjunction with pulping to be considerably less likely to form disturbance residuals that cause serious problems in the recycling of paper products treated with synthetic adhesives. In extreme cases, the amount of synthetic monomers can be low - even
30 nil. Actually, the properties of a dispersion manufactured in this manner are impaired in that the coater substance's adhesion is low but still such a dispersion may find use in less demanding situations.

35 As is pointed out in the above, applications for dispersions manufactured in accordance with the invention are mainly in conjunction with packaging materials and wrap-

5 pings that are required to possess certain moisture and vapour barrier properties. In these cases the dispersion can be used in place of conventional plastic/paper lamination solutions that are non-recyclable as well as being very slowly degradable in nature on the part of their plastic component.

10 When dispersions manufactured in accordance with the present invention are used, the resultant paper products degrade relatively quickly in nature. When compared to products made using fully synthetic latexes, the degradability of products treated with dispersions manufactured in accordance with this invention is also better because the starch components contained by the dispersion and polymer structure offer a natural substrate for
15 naturally occurring decomposing hydrolytic enzymes. A polymer dispersion offering better recycling and degrading properties, and manufactured in the manner described in the above, has reasonable barrier properties to offer as such. When necessary, the vapour barrier properties can be further modified by means of additives
20 such as a wax dispersion.

25 The following is a description of ways according to which polymers forming the structure of the dispersion can be manufactured.

(A) Manufacturing of latex containing starch in a polymer structure.

30 The principle here is that the reaction medium used in the manufacturing of latex by means of the emulsion polymerization method is a water solution containing conventional additives such as initiators acting as catalysts (persulphates, peroxides) and surface-active substances and starch dissolved into the water phase by
35 heating. When this is the case, the initiators cause

radicals to form onto the starch structure and these radicals then act as the initial centres of the polymerization reaction. In other words, in addition to the fully synthetic material formed in normal emulsion polymerization, one obtains starch graft copolymer material in which the polymer chains formed of the synthetic monomers used are covalently attached to the starch structure.

Since native starch - regardless of its origin - is a macromolecular compound and water solutions of it have very high viscosities even in very low solid matter concentrations, one must first reduce the molecular size of the starch or better still use commercially available starch qualities which have usually been split up by means of oxidization. In the event that the user wishes to carry out the oxidization-based splitting up in conjunction with the reaction, this can be done using a known art method advantageously as the first stage in the reaction by using the oxidizing initiators acting as polymerization catalysts.

In order that the viscosity of the polymer dispersion obtained as the end product might fall within the appropriate range and that it might be a replicable constant, one must take great care to ensure that the degree of splitting of the starch is always precisely that which is required. This can be done by means of viscosity determination, end group analysis or gel permeation chromatography. The initial starch used in the following examples is either a commercial, hydrogen peroxide oxidized potato starch Raisamyl 302P with a viscosity of 20-30 mPas when used as a 10% solution at a temperature of 60 °C or native potato starch that has been split up enzymatically by alpha-amylase possessing temperature stability with respect to *Bacillus licheniformis* in the manner described in the example.

Example 1:

(A1) 34.30 g of oxidized starch Raisamyl 302P were added to 150 g of water and then transferred into a pressure-proof reactor vessel. The temperature of the mixture was raised to 100 °C for a period of 20 minutes in order to dissolve the grains of starch. Following this the mixture was cooled down to 70 °C after which a solution containing 2.5 g of sodium lauryl sulphate in 50 ml of water. A monomer mixture containing 116.8 g of styrene, 73.9 g of butadiene washed with a solution of lye and 3.0 g of acrylic acid were then gradually added to the mixture over a period of two hours. Initiator solution containing 3.0 g of ammonium persulphate in 70 g of water was added from another pressure burette. The polymerization reaction was then allowed to proceed for 12 hours. The end product was a white dispersion with a solid matter concentration of 45.8% and a viscosity of 890 mPas as measured by a Brookfield LVT viscometer using measuring head no. 2 at 2100 r/min. The measurements were conducted after the product had been neutralized with NaOH to a pH of 6.8. The product's calculatory starch concentration was 13%.

Example 2:

(A2) 34.5 g of oxidized starch were added to 150 g of water and boiled for 20 minutes in order to dissolve the grains of starch. Following this 2.5 g of sodium lauryl sulphate in 50 ml of water were added to the solution as was the catalyst solution and the monomer solution as mentioned in connection with Example 1. The composition of the monomer solution in this case was 146 g of vinyl acetate and 22 g of butyl acrylate. The reaction was allowed to proceed for 14 hours. The dry matter concentration of the neutralized product was 40.8% and its viscosity was 600 mPas at a temperature of 25 °C.

Example 3: 49.4 g of oxidizer starch were added to 370 g of water and boiled for 20 minutes in order to dissolve the grains of starch. The reaction mixture was provided with an inert atmosphere by means of a flow of nitrogen. Next, 0.1 g of CuSO_4 was added followed by the addition during a period of 1.5 hours of a monomer mixture composed of 75 g of acrylic acid and 53 g of acrylic nitrite in drops. This was accompanied by the concurrent addition to the reaction mixture of 6 g of 30% hydrogen peroxide given over a period of 2 hours. The reaction was allowed to proceed for 11 hours at a temperature of 70 °C. The product thus obtained was a white dispersion with a dry matter concentration of 26.3%.

15

Example 4:

(B1) Starch copolymer production. 250 g of native potato starch with a moisture content of 16% were mixed into 220 g of water. This was followed by adding 0.05 U/g of starch of alpha-amylase possessing a temperature stability with respect to *B. licheniformis* and with an activity value of 984 U/ml. While mixing the suspension vigorously, its temperature was raised to 90 °C and kept there for 30 minutes. As a means of stopping enzymatic activity 0.5 ml of 30% hydrogen peroxide was added and the temperature was brought down to 60 °C. A flow of nitrogen was led into the reaction mixture, 0.2 g of CuSO_4 were added, and 38 g of styrene and 6 g of 30% hydrogen peroxide were administered in drops at the same time for a period of 1.5 hours. The reaction was allowed to proceed for another 2 hours at the end of which the resultant white dispersion was cooled down to room temperature. The dispersion's viscosity at 25 °C was 670 mPas and its solid matter concentration was 51.8%.

35

Example 5:

(B2) Starch graft polymer was produced in the manner described in Example 3 above using butyl acrylate (75 g) as the monomer to be grafted. The amount of starch was 209 g and it was added to 217 g of water. The resultant product was a yellowish dispersion with a room temperature viscosity of 610 mPas and a solid matter concentration of 50.5%.

Example 6:

This example describes the compositions of the formulations finally spread onto paper surface, containing dispersions according to examples 1-4 and control formulations and the properties of papers treated with them. LD460 is a styrene butadiene latex, manufactured by Raison Lateksi Oy, RN1125 is a vinyl acetate acrylate latex, manufactured by Rasional Oy, vahad is a wax dispersion containing paraffin with a melting range of c. 50-70 °C.

Using a laboratory coater machine (Endupapp), the dispersion was spread onto board (grammage 190 g/m²). The board was then measured for its water vapour permeability (WWP) in accordance with the ISO 258-1974 method (unit: g/m²/24h). PM= amount of dispersion spread (g/m²).

The value PA in the table depicts the pulpability properties of treated board. The value is obtained as follows: the treated board was broken down in accordance with the method SCAN-C 18:65. The pulped material was made into laboratory sheets (grammage: c. 100 g/m²). The sheet quality was assessed using a scale of 0 - 5 in which 0 indicates good pulpability (no accumulations of surface treatment material observed) and 5 indicates poor pulpability (numerous accumulations of surface treatment substance or unevenness due to incomplete breaking down

of material).

Table 1.

		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11
5	LD460	100	-	-	-	-	70	70	60	90	-	-
	RN1125	-	100	-	-	-	-	-	-	-	-	-
	A1	-	-	100	90	-	-	-	-	-	-	-
	A2	-	-	-	-	100	-	-	-	-	-	-
	A3	-	-	-	-	-	100	-	-	-	-	-
10	B1	-	-	-	-	-	-	30	-	30	-	-
	B2	-	-	-	-	-	-	-	30	-	-	-
	vahad	-	-	-	10	-	-	-	-	10	10	-
15	PM	17.8	20.2	19.9	18.7	21.0	20.3	19.4	20.3	20.1	18.0	0
	WWP	29	98	32	7	36	4	27	38	8	5	151
	PA	5	3	2	2	0	0	1	1	1	4	0

20

Example 7:

In this example two pieces of board are made into a laminated product by means of a dispersion manufactured in accordance with the invention. Dispersions R3, R6 and R8 were spread onto boards using amounts that corresponded to c. 20 g/m² of solid matter. Immediately after this step another sheet of the same board was pressed against the treated surface and the thus formed laminated product was then allowed to dry. The outcome of the gluing operation was assessed on the basis of the fibre tear produced when the two layers were separated from one another (total fibre tear = excellent adhesion). The laminates were also measured for their vapour barrier values.

35

Table 2.

		Fibre tear	WWP (g/m ² /24h)
40	R3	Total	29
	R6	Total	9
	R7	Total	28
	R9	Almost total	12

PATENT CLAIMS:

1. A method for reducing the permeability of paper or board by coating paper or board with a coater consisting of one or more polymer dispersions, **characterized** in that the polymer dispersion used in the coater substance contains a component containing modified starch.
2. A coater substance for a method as claimed in claim 1, **characterized** in that the component containing starch has been prepared by emulsion polymerization of dissolved, split up starch in water phase by means of a monomer mixture by feeding the monomer mixture into a water phase containing 2-25% of starch as calculated from the finished dispersion's solid matter.
3. A coater substance as claimed in claim 2, **characterized** in that the polymer dispersion's starch-containing component has been prepared using a monomer mixture containing styrene and butadiene as its main components.
4. A coater substance as claimed in claim 2, **characterized** in that the starch-containing component of the polymer dispersion has been prepared using a monomer mixture containing esters of vinyl acetate and acrylic acid and lower alcohols (methyl, ethyl, propyl or butyl) as its main components.
5. A coater substance as claimed in claim 2, **characterized** in that the polymer dispersion's starch-containing component has been prepared using a monomer mixture containing acrylic acid and acryl nitrate as its main components.
6. A coater substance as claimed in claim 1, **characterized** in that the polymer dispersion's starch-containing component has been prepared by grafting to the split up

starch unsaturated monomer in amounts corresponding to 0-50% of the amount of starch.

5 7. A coater substance as claimed in claim 6, **characterized** in that the polymer dispersion's starch-containing component has been produced by grafting a styrene monomer onto split up starch.

10 8. A coater substance as claimed in claim 6, **characterized** in that the polymer dispersion's starch-containing component has been prepared by grafting onto the split up starch an ester monomer formed of acrylic acid and lower alcohols.

15 9. A coater substance for reducing the permeability of paper or board, **characterized** in that it contains a polymer dispersion containing 10-100% of starch-containing polymer component and 0-90% of a starch-free component and 0-30% of a wax dispersion.

20 10. A coater substance as claimed in claim 9, **characterized** in that the starch-free polymer dispersion is styrene butadiene latex.

25 11. A coater substance as claimed in claim 9, **characterized** in that the starch-free polymer dispersion is vinyl acetate - acryl latex.

30 12. A coater substance as claimed in claim 9, **characterized** in that the melting point of the wax used in the dispersion is c. 50-70 °C.

35 13. A method as claimed in claim 1, **characterized** in that the coater substance is spread between two or more paper and/or board layers and that the layers are bound to one another using the coater substance.

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AMENDED CLAIMS

[received by the International Bureau on 21 April 1993 (21.04.93);
original claims 1 and 5 amended; other claims unchanged (2 pages)]

1. A method for reducing the gas and vapour permeability of paper or board by coating it with a coater consisting of one or more polymer dispersions, characterized in that the polymer used in the coating dispersion at least partly consists of modified starch.
2. A coating substance for a method as claimed in claim 1, characterized in that the component containing starch has been prepared by grafting of dissolved, split up starch in water phase by means of a monomer mixture by feeding the monomer mixture into a water phase containing 2-25% of starch as calculated from the finished dispersion's solid matter.
3. A coating substance as claimed in claim 2, characterized in that the polymer dispersion's starch-containing component has been prepared using a monomer mixture containing styrene and butadiene as its main components.
4. A coating substance as claimed in claim 2, characterized in that the starch-containing component of the polymer dispersion has been prepared using a monomer mixture containing esters of vinyl acetate and acrylic acid and lower alcohols (methyl, ethyl, propyl or butyl) as its main components.
5. A coating substance as claimed in claim 2, characterized in that the polymer dispersion's starch-containing component has been prepared using a monomer mixture containing acrylic acid and acryl nitrile as its main components.
6. A coating substance as claimed in claim 1, characterized in that the polymer dispersion's starch-containing component has been prepared by grafting to the split up

starch unsaturated monomer in amounts corresponding to 0-50% of the amount of starch.

5 7. A coating substance as claimed in claim 6, characterized in that the polymer dispersion's starch-containing component has been produced by grafting a styrene monomer onto split up starch.

10 8. A coating substance as claimed in claim 6, characterized in that the polymer dispersion's starch-containing component has been prepared by grafting onto the split up starch an ester monomer formed of acrylic acid and lower alcohols.

15 9. A coating substance for reducing the permeability of paper or board, characterized in that it contains a polymer dispersion containing 10-100% of starch-containing polymer component and 0-90% of a starch-free component and 0-30% of a wax dispersion.

20 10. A coating substance as claimed in claim 9, characterized in that the starch-free polymer dispersion is styrene butadiene latex.

25 11. A coating substance as claimed in claim 9, characterized in that the starch-free polymer dispersion is vinyl acetate - acryl latex.

30 12. A coating substance as claimed in claim 9, characterized in that the melting point of the wax used in the dispersion is c. 50-70 °C.

35 13. A method as claimed in claim 1, characterized in that the coating substance is spread between two or more paper and/or board layers and that the layers are bound to one another using the coating substance.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 92/00305

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21H 19/34, D21J 1/08, C09D 5/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21H, D21J, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP, A2, 0307795 (MD-PAPIERFABRIKEN HEINRICH NICOLAUS GMBH), 22 March 1989 (22.03.89), claim 1	1
X	US, A, 4585501 (STEVEN D. OVERHOLT), 29 April 1986 (29.04.86), column 2, line 46 - line 53, claim 1	1, 13
A	column 2, line 25 - line 53	2, 3, 9
X	EP, A1, 0404582 (MERCK & CO. INC), 27 December 1990 (27.12.90), page 2, line 6 - line 15; page 2, line 1 - line 35	1

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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23 February 1993

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4109056 (GERALD CRAIG ET AL), 22 August 1978 (22.08.78), abstract	1
A	--	3
A	EP, A2, 0319846 (ENSO-GUTZEIT OY), 14 June 1989 (14.06.89), claims 1,7, abstract	1
A,P	Orbit Search Service, File WPAT, Accession number 92-273034/33, SUMITOMO CHEM CO LTD: "High resistant, waterproof paper coating compsn. - comprise pigments, aq. binders and water insol.- substd. benzoxazolyl: thiophene fluorescent whitening agents", JP04185797-A, 920702, 9233, abstract	1,2,3
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INTERNATIONAL SEARCH REPORT
Information on patent family members

29/01/93

International application No.
PCT/FI 92/00305

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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